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Project Summary

Treatability Studies of Pesticide Manufacturing Wastewaters

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Laboratory and pilot studies of the treatability of pesticide manufacturing wastewaters were conducted in a project designed to investigate the suitability of individual pesticide manufacturing wastewaters for discharge to biological treatment systems, whether publicly owned treatment works (POTWs) or on-site systems. The pesticides studied were carbaryl, dinoseb, atrazine, dazomet, glyphosate, and an ethylenebisdithiocarbamate fungicide.

The approach taken with each pesticide manufacturing wastewater was prioritized; that is, less costly, more available methods of treatment were investigated first. The preferred method of treatment was assumed to be biological. The suitability of the pesticide wastewater for direct biological treatment was based on chemical and toxicological evaluation of the waste after treatment. Where information was available on actual dilution rates upon entering biological treatment facilities, these rates were used in the evaluation. If the waste was judged suitable for biological treatment, additional treatment options were not evaluated.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in five separate reports (see Project Report ordering information at back).

Introduction

In Feburary 1979, Research Triangle Institute (RTI) was requested by EPA's Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP), NC, to conduct laboratory and pilot studies of the treatability of a number of pesticide manufacturing wastewaters. The project was designed to investigate the suitability of individual pesticide manufacturing wastewaters for discharge to biological treatment systems, whether publicly owned treatment works (POTWs) or on-site systems.

Six pesticides were selected for study. Their chemical structures are given in Figure 1. Factors influencing selection were:

(1) Potential for continued use of the pesticide.
(2) Production of a significant liquid waste stream.
(3) Large annual production and widespread use.
(4) Chemical class; i.e., representatives of several types of chemical structures.
(5) Availability of the wastewater: i.e., interest of the manufacturers in cooperating with the study.
(6) Present treatment of wastewater; i.e., wastewaters now deep-well-

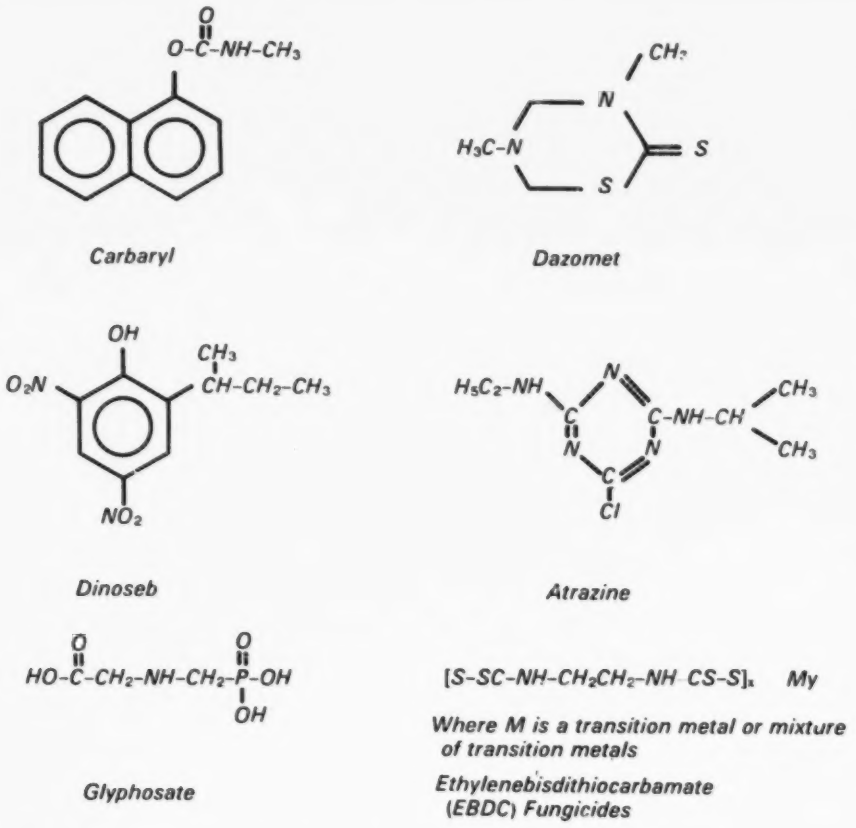

Figure 1. *Chemical structures of pesticides studied.*

injected or contract-hauled were considered because of the potential for groundwater contamination with present disposal methods.

Carbaryl is a wide-spectrum insecticide for control of insects on cotton, vegetables, fruit, rice, sugarcane, and ornamentals. Atrazine is a registered herbicide used for pre- and post-emergence weed control on numerous crops including corn, sorghum, sugarcane, and nursery conifers; it is recommended for use in fish ponds for selective control of farm pond weeds, especially submerged aquatics. Dinoseb is a general-contact weed killer for both pre- and post-emergence control. Glyphosate is a post-emergent herbicide registered with the EPA for the control of annual and perennial weeds before the emergence of agronomic plants. It is also effective in controlling ditch bank vegetation. Maneb-type ethylenebisdithiocarbamate (EBDC) fungicides are used to control foliar fungal blights. It is recommended for prevention of early and late blight on tomatoes and potatoes and can be combined with other fungicides for persistent fungal strains. EBDC fungicides are used to control over 400 fungal diseases for protection of over 70 crops.

Treatability Studies

The approach taken with each pesticide manufacturing wastewater was hierarchical; that is, less costly, more available methods of treatment were investigated first. The preferred method of treatment was assumed to be biological. The manufacturing wastewaters first were characterized for their pesticide content and for routine wastewater parameters, including toxicity to fish, algae, and activated sludge. They were then subjected to bench-scale continuous activated sludge (AS) treatment using the complete-mix continuous-feed units designed by Swisher (1970) and/or those designed by the Organization of Economic Cooperation and Development (O.E.C.D.) (Bundegesetzblatt, 1977). These units are made entirely of glass, avoiding the possibility of contamination by organics leaching from the containers. Continuous feed to the units was supplied through Teflon tubing by a peristaltic pump.

Routine determinations were made of dissolved oxygen, pH, mixed liquor volatile suspended solids in the aerator, COD, and pesticides in the influent and effluent. Dissolved oxygen was determined with an oxygen probe (Yellow Springs Instrument Company).

If pesticide manufacturing wastewater disrupted biological treatment systems, despite gradual increase of concentration and acclimation, the possibility of preheating the waste prior to biological treatment was investigated. Pretreatment included pH adjustments, filtration, flocculation, and oxidation, depending on the nature of the wastewater and its chemical composition.

If pretreatment did not improve the performance of activated sludge systems, adsorption techniques were investigated, involving both carbon and resin systems. Physical-chemical treatability of wastewaters was then evaluated again with the biological treatment system (i.e., removal of toxicity and of constituents of interest).

Conclusions and Recommendations

Carbaryl

Based on the results of the bench-scale experimental work in this study, both carbaryl manufacturing wastewater, when mixed 1 part in 9 parts municipal wastewater, and carbaryl itself, when spiked at 10 mg/L in municipal wastewater, appear suitable for biological treatment by acclimated systems if additional provision is made for removing ammonia in the effluents from the biological treatment system. Other parameters investigated in this study—including carbaryl, α-naphthol, and toluene concentrations—and chemical oxygen demand (COD) showed large reductions (90 percent or greater). The mechanisms of reduction of these parameters include combined hydrolysis and biodegradation of carbaryl and α-naphthol, volatilization of toluene, and biodegradation of species contributing to COD.

A large increase in ammonia concentration was noted in the effluent from the biological treatment units relative to their influent. This ammonia concentration made the toxicological evaluation of the effectiveness of treatment problematic by rendering the effluent more toxic than the influent. Ammonia stripping lessened this toxicity. Because the technology of nitrogen control has been extensively developed, these treatment options were not pursued further.

The carbaryl manufacturing wastestream investigated in this study is now mixed with other manufacturing wastestreams and treated in a manufacturer-operated aerated lagoon with approximately a 3-day retention time. Based on the study, this treatment process should be adequate for the carbaryl manufacturing wastestream if there is no interference from the components of other wastestreams and if nitrification of ammonia occurs.

Dinoseb and Atrazine

The effluent from the manufacture of dinoseb and atrazine proved suitable for a treatment system involving preliminary activated carbon filtration to remove the herbicide, followed by biological treatment to reduce oxygen demand exerted by solvents and other organic compounds. Several other treatment systems were tried but were not successful. These alternatives included biological treatment of the manufacturing wastes diluted in municipal wastewater. This system provided some reduction in chemical oxygen demand (COD) of the waste. However, both the dinoseb and the atrazine levels were unaffected.

A pretreatment system involving the hydrolysis of pesticide manufacturing wastes was tried. This system greatly reduced the phytotoxicity of the wastes as measured by the algal bioassay. However, subsequent biological treatment of this waste provided only a marginal reduction in the hydroxyatrazine byproducts of the hydrolysis reaction.

Activated carbon filtration alone greatly reduced the phytotoxicity of the pesticide manufacturing wastes. Substantial breakthrough of other organic compounds (e.g., solvents such as acetone) was seen before any breakthrough of either of the pesticides from the carbon column. This COD content was then further reduced in a biological treatment system through the mechanisms of volatilization and biological degradation. Biological treatment reduced the phytotoxicity of these wastes below that seen with activated carbon treatment alone.

The volatile nature of the organic constituent of this waste could allow consideration of air-stripping as a viable treatment option after carbon treatment. Additional work would be necessary to determine the effluent quality achievable with air-stripping and the nature of the stripped organics.

A report has been made of the formation of nitrosamines in excess of 200 ppm in the formulation of dinoseb as a diethanolamine salt (Bontoyan, Law, and Wright, 1979). While the formulation of dinoseb is not expected to generate an aqueous wastestream, care should be taken in any washup or rinsing procedure after formulation. Monitoring for various nitrosamines is recommended if there is reason to believe that there is a source of input of these nitrosamines into the main plant wastestream.

Dazomet

The effluent from the manufacture of dazomet was tested for treatability by activated sludge systems when diluted 1:100, 1:500, and 1:1000 in municipal wastewater. At 1:100 dilutions, dazomet concentrations showed over 95 percent reduction after biological treatment. However, effluent COD levels were unacceptably high at an average of 160 mg/L. At 1:500 levels, the effluent COD was much closer to the control effluent. However, nitrification of ammonia was severely hampered. At 1:1000 dilutions, the dazomet wastewater had a variable effect on nitrification while effluent COD levels were close to controls. It is recommended that dazomet wastewater be diluted to at least 1:1000 in municipal wastewater to minimize the negative effects on the nitrification of ammonia during the activated sludge treatment process.

No difference in toxicity in bioassay tests was noted in effluents from activated sludge units fed 1:500 or 1:1000 dilutions and units fed municipal wastewaters alone.

Pretreatment of the dazomet wastewater by air-stripping under alkaline conditions (pH 11) reduced the dazomet concentrations but had no effect on the COD or ammonia concentration. Air-stripping at low pH was not attempted due to the generation of toxic carbon disulfide under these conditions.

Glyphosate

Various combinations of glyphosate production wastestreams were subjected to biological treatment following lime-pretreatment to reduce high levels of glyphosate. Bench-scale biological treatment demonstrated that glyphosate did not appear to interfere with the biological degradation process at concentrations up to 105 mg/L. On the other hand, glyphosate itself showed only partial reduction with biological treatment (28 to 45 percent). The mechanism of this removal is not fully understood but may include sorption to sludge. No evidence for metabolism of glyphosate was generated in oxygen uptake studies. While the test does not provide any evidence for metabolic uptake of glyphosate, it is also interesting that fairly high concentrations of the compound do not inhibit other microbial processes in acclimated sludge.

Biological treatment significantly reduced the toxicity of these effluents. Test data clearly show that the higher toxicity in influents versus effluents is not due to glyphosate itself but to other wastestream components, many of which are effectively treated in an activated sludge process. The toxicity of glyphosate was found to depend on water quality parameters such as calcium and magnesium concentration; toxicity decreased as water hardness increased. Glyphosate was more toxic in soft water than similar concentrations of glyphosate in the effluents from biological treatment systems. The decreased toxicity in effluents is probably related to the addition of calcium in the lime pretreatment step.

Additional treatment options were investigated in an attempt to reduce glyphosate concentrations in the influents to biological treatment. These options, including ozonation, adsorption, and ion exchange, provided only marginal reduction of glyphosate.

Ethylenebisdithiocarbamate (EBDC) Fungicides

At levels representative of their concentration in the influent to the POTWs, neither the wastewater from the EBDC production unit nor the total plant wastewater affected the ability of pilot activated sludge units to remove COD. At these levels, the presence of both wastewaters strongly inhibited nitrification in activated sludge units, as

compared to control units fed typical domestic wastewater alone.

Biological treatment decreased, but failed to eliminate, the amount of ethylenethiourea (ETU), a decomposition product of the pesticide, in the wastewaters. Nitrification and ETU removal were superior in activated sludge units inoculated with sludge from a plant treating domestic wastewater, compared to units inoculated with sludge from the POTW receiving the pesticide wastewater. Nitrifying bacteria are known to be inhibited by thioureas. These findings possibly indicate that continued exposure of sludge to the EBDC wastewaters can reduce the bacterial populations responsible for nitrification and for ETU removal.

Results of bioassays in the two wastewaters showed inhibition of growth and mobility characteristics. Metals analysis indicated that this toxicity could be due in part to the presence of Mn and Zn. If so, removal of these metals might be investigated as a means of relieving the toxicity of the wastewaters to aquatic organisms. Note, however, that at dilutions representative of actual conditions at the receiving POTW neither wastewater exhibited much toxicity.

Future studies should be conducted to define the effects of ETU and EBDC fungicides on nitrification, since this process, either in a POTW or in a receiving stream, is critical to maintenance of the nitrogen cycle. The public health significance of ETU in the activated sludge effluents should also be investigated.

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***David C. Sanchez** is the EPA Project Officer (see below).*

The complete report consists of five volumes, entitled "Treatability Studies of Pesticide Manufacturing Wastewaters":

Carbaryl (Order No. PB 80-224 306; Cost: $6.50, subject to change)
Dazomet (Order No. PB 81-129 033; Cost: $6.50, subject to change)
Dinoseb and Atrazine (Order No. PB 81-178 840; Cost: $6.50, subject to change)
Glyphosate (Order No. PB 81-159 097; Cost: $8.00, subject to change)
Ethylenebisdithiocarbamate Fungicides (Order No. PB 82-107 566; Cost: $9.50, subject to change)

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